AD-A255 992

CUMENTATION PAGE

ation is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, noleting and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson 2. and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
AUG 31, 1992	Final, Phase 1 --- April 1991-April 1992

4. TITLE AND SUBTITLE
Radical Ion Formation in polymers as a mechanism for Laser Eye Protection

5. FUNDING NUMBERS
(C) DAAK60-91-K-0002

6. AUTHOR(S)
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OCT 2 1992
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Worcester Polytechnic Institute
Worcester MA 01605

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
ARO U.S. Army Research Deveploment and Engineering
Center, Natick, MA

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Phase 1 of this contract involved the synthesis of several representative compounds containing organic chromophores which are capable of donating and accepting a single electron after two-photo excitation. The selection of suitable chromophores was based on a set preset criteria which is listed in the contract proposal. The suitability of these chromophores for the stated application was determined first by studying their spectroscopic and electron transfer properties as separate molecules in solution (i.e. intermolecular). Once the intermolecular behavior of these chromophores was evaluated, synthesis of molecules incorporating both the donating and accepting chromophores was carried out. This report describes the following work: i) spectroscopic evaluation of the two-photon-induced intermolecular electron donor/acceptor abilities of the chosen chromophores; ii) synthesis of molecules incorporating both the electron donating and accepting chromophores; iii) preliminary spectroscopic investigation in solution of the synthesized molecules.

14. SUBJECT TERMS
1) LASER EYE PROTECTION
2) RADICAL IONS

15. NUMBER OF PAGES
29

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASS.	UNCLASS.	UNCLASS.	

Standard Form 298 (Rev 2-89)

JK 9/30/92

Cover Sheet

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DTIC QUALITY INSPECTED 3

Contract #: DAAK 60-91-K-0002

Title: Radical Ion Formation in Polymers as a Mechanism for Laser Eye Protection

Date: August 31, 1992

Subject: Final Report - Phase I.

92 9 25 034

92-25936

425592

Radical Ion Formation in Polymers as a Mechanism for Laser Eye Protection

Research Contract: **DAAK60-91-K-0002**

Final Report, Phase 1.

Phase 1 of this contract involved the synthesis of several representative compounds containing organic chromophores which are capable of donating and accepting a single electron after two-photon excitation. The selection of suitable chromophores was based on preset criteria which were listed in the contract proposal. The suitability of these chromophores for the stated application was determined first by studying their spectroscopic and electron transfer properties as separate molecules in solution (i.e. under intermolecular conditions). Once the intermolecular behavior of these chromophores was evaluated, synthesis of molecules incorporating <u>both</u> the donating and accepting chromophores was carried out. This report describes the following work: i) spectroscopic evaluation of the two-photon-induced intermolecular electron donor/acceptor abilities of the chosen chromophores; ii) synthesis of molecules incorporating both the electron donating and accepting chromophores; iii) preliminary spectroscopic investigation in solution of the synthesized molecules.

I. Spectroscopic Investigations of Two-Photon Intermolecular Electron Donor/Acceptor Pairs.

The first section describes the two-photon-induced electron transfer between anthracene and a variety of electron acceptors. The chemistry of the anthracene T_2 state in room temperature acetonitrile solution in the presence of a variety of quenchers has been investigated by two-laser flash photolysis. The decay of T_2 in the presence of ethyl bromoacetate, which is capable of undergoing reductive dehalogenation, is via electron transfer as evidenced by the detection of the anthracene radical cation, λ_{max} 720 nm. Indirect evidence shows that in benzonitrile, T_2 decay is primarily by electron transfer with a minor contribution due to energy transfer (T_2 -> benzonitrile S_0). The failure to detect the cation radical, even in the presence of an applied magnetic field, indicates that cage escape cannot compete kinetically with ISC followed by back electron transfer in the geminate radical ion pair. T_2 reacts with acrylonitrile and fumaronitrile partially via 4+2 cycloaddition at the anthracene 9 and 10 positions. Again, indirect evidence suggests that triplet-triplet energy transfer and electron transfer also contribute to T_2 decay.

Introduction

The ability of upper excited triplet states to decay by photophysical pathways other than $T_2 \to T_1$ internal conversion has been recognized for some time. Early product studies showed that CW irradiation of anthracene in the presence of *trans*,-stilbene resulted in *trans-cis* isomerization. Spectroscopic studies at low temperatures involving excitation of anthracene in the presence of naphthalene resulted in naphthalene phosphorescence emission. In both cases, the observed behavior was attributed to intermolecular energy transfer from anthracene T_2 to the substrate.

More recently, time-resolved two-color (two-laser) studies have shown that a variety of aromatic hydrocarbons and ketones have T_2 reactivity and that in addition to energy transfer, Norrish Type I cleavage, debromination, and reverse intersystem crossing are all possible T_2 deactivation pathways.

As it turns out, anthracene and anthracene derivatives are especially well suited for the study of upper triplet decay processes. The T_1 and T_2 energies are ~40[12] and ~74 kcal/mol, respectively, and this large energy gap contributes to a relatively long T_2 lifetime (t~200 ps). It is this long lifetime that allows efficient (diffusion-controlled) intermolecular processes to compete effectively with internal conversion.

To date, with the exception of energy transfer, there have been few reports of intermolecular reactions involving T_2 states. Given the fact that the T_2 state of anthracene is long-lived and nearly isoenergetic with the S_1 state, and that S_1 participates in a wide variety of chemical processes including electron transfer, 4+2 cycloaddition, and dimerization, it was believed that the T_2 state could also participate in these reactions.

We report here the two-laser flash photolysis study of anthracene in the presence of ethyl bromoacetate, benzonitrile, acrylonitrile and fumaronitrile, all of which are capable, thermodynamically, of oxidizing anthracene T_2. In addition to electron transfer, we have found that T_2 participates in energy transfer and cycloaddition.

Experimental

Materials: All chemicals and reagents were obtained from Aldrich unless specified otherwise. Acetonitrile, benzene and benzonitrile were Spectrophotometric grade and were used as received. Acrylonitrile (99+ %) was also used as received. Ethyl bromoacetate (98 %), 1,2-dimethoxybenzene (99 %) and fumaronitrile (98 %) were distilled prior to use. Anthracene was recrystallized from ethanol. The structures of the compounds used are given below.

$$CH_2 = CHCN \qquad CNCH = CHCN$$

Acrylonitrile   (AN)   Fumaronitrile   (FN
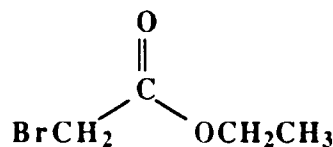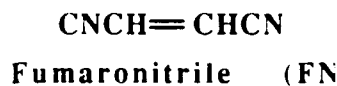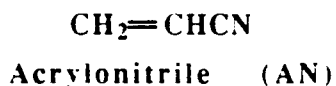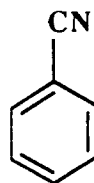
Ethyl bromoacetate   (EBA)   Benzonitrile   (BN)
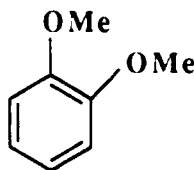
1,2-Dimethoxybenzene   (DMB)

Absorption and Fluorescence Spectroscopy: Absorption spectra were obtained with a Shimadzu 2200 UV-Vis dual beam spectrophotometer using 7x7 mm^2 quartz cells with pure solvent as reference. Fluorescence emission spectra were obtained with a Perkin-Elmer LS50 spectrofluorimeter. Samples were dilute in order to minimize the effects of self absorption.

Laser Flash Photolysis: Apparatus: Three pulsed lasers were used as excitation sources. UV excitation was provided by either a Lumonics EM510 XeCl excimer laser (308 nm, 30 mJ/pulse, 8 ns pulse duration) or by the frequency tripled output of a Continuum "Surelite" Nd/YAG laser (355 nm, <50 mJ, 6 ns). Visible excitation was provided by a Candela SLL 250 flashlamp-pumped dye laser (420-700nm, < 250 mJ, 350 ns). The monitoring system consisted of a pulsed 150W xenon lamp as the light source, an Acton Research Corp. 27.5-cm focal length microprocessor-controlled monochromator equipped with two gratings -- a wavelength-neutral holographic grating and a conventional grating blazed at 750 nm for enhanced red sensitivity-- with a six stage Burle 4840 photomultiplier attached to the exit slit. Signal capture was by a Tektronix 7912 HB transient digitizer. I_0 values were obtained by a home-built sample and hold unit, which also provided a DC offset to the signal, and were transferred to the computer through a Sciemetric Labmate Intelligent Lab Interface. The Labmate was also used to control the photomultiplier voltage as well as electronic shutters in the path of the laser and monitoring beams.

The monitoring lamp pulser, digitizer, lasers and sample and hold unit were all triggered with a Stanford Research Systems digital delay pulse generator which provided variable amplitude, independently delayed TTL pulses which allowed synchronisation and gating of each instrument. The pulse generator, monochromator, Labmate and digitizer were interfaced (RS-232,

GPIB parallel bus) to an AT&T 80286 PC responsible for both execution of the data acquisition programs and data analysis.

Sample Preparation: Samples in a typical experiment were either static (7x7 mm^2 quartz cells - 3 ml volume) or were flowed through a specially constructed quartz flow cell which ensures that a fresh volume of sample is irradiated by each laser pulse. The optical density of samples at the laser wavelength was < 0.5. All samples unless otherwise noted were outgassed with dry nitrogen.

Product Studies: Product studies were carried out using GC and GC-MS analysis of static samples which had been subjected to two-laser irradiation. A continuously degassed sample was irradiated by approximately 500 pairs of laser pulses (UV pulse followed by dye laser pulse after a 0.75 - 1 μs delay). A control experiment was also performed in which the sequence of the lasers was reversed, thus allowing the effects of the UV pulse alone to be measured.

Synthesis of dibenzobicyclo[2.2.2]octa-5,7-diene-2-carbonitrile (4+2 cycloaddition product): A solution of 10g of anthracene and 4 mL acrylonitrile in 20 mL xylene was heated in a sealed bomb at 170 C for 8 hr yielding the cycloaddition product, I, in ca. 75 % yield. It was subsequently recrystallized from ethanol and identified by GC-MS.

I
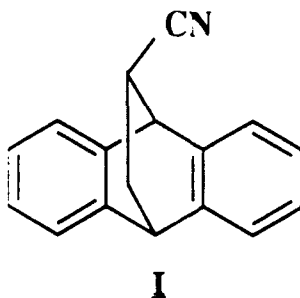
Results and Discussion

Two-Laser Photochemistry of Anthracene Alone. Irradiation of a degassed solution of anthracene (1mM) in acetonitrile (MeCN) by either a 308 nm excimer laser or 355 nm frequency-tripled YAG laser resulted in the production of the anthracene triplet state, T_1, detected by its T-T absorption spectrum (λ_{max} 425 nm). The formation of the T_1 states of anthracenes is known to proceed via $S_1 \rightarrow T_2$ ISC followed by T_2-T_1 relaxation. In addition to the T-T absorption, a second, minor absorption band was detected with λ_{max} 720 nm. This weak transient absorption, which decays by mixed first and second order kinetics, is assigned to the anthracene radical cation based on literature values obtained by photochemical and electrochemical techniques. Support for this assignment is also given by the fact that the absorption band at λ 720 nm is absent in nonpolar solvents such as cyclohexane, i.e. the radical cation is stabilized in acetonitrile. In addition, the absorption was quenched at nearly a diffusion controlled rate (k_q= 9.3 x $10^8 M^{-1} s^{-1}$) by the addition of tetra-n-butylammonium bromide (bromide acts as a cation scavenger).

Suppan and coworkers have attributed radical cation formation, which they also found to be inefficient, to monophotonic ionization of anthracene S_1 followed by solvation of the ejected electron by MeCN. Since the ionization is endergonic by ca. 8 kcal/mol, it is not surprising that radical cation formation is inefficient. In fact, it is possible that trace concentrations of water, which is present in even the most rigorously purified MeCN, may account for the majority of radical cation formation observed in their experiments as well as our

own. This would appear to be confirmed by our observation of an increased yield of radical cation when 9:1 MeCN:H_2O was used as solvent.

Irradiation of the triplet state by a pulsed flashlamp-pumped dye laser tuned to the T-T absorption band (λ_{dye}=445 nm) ca. 1 μs after the initial UV pulse caused no observable change in the triplet decay kinetics or the transient absorption spectrum. While excitation of T_1 with 445 nm photons initially produces an upper excited triplet state, T_n, with energy in excess of 100 kcal/mol, relaxation of T_n to T_2 is expected to be faster than any alternative intramolecular decay pathway such as photoionization, or intermolecular process involving the solvent. Relaxation from T_2 (E=74 kcal/mol), is slower than from upper triplet states due to the large T_2-T_1 energy gap (ca. 34 kcal/mol), resulting in a relatively long T_2 lifetime (τ=200ps).

Although inter- and intramolecular decay processes other than relaxation have been reported for upper states with comparable lifetimes, for anthracene T_2 in MeCN the thermodynamics and/or kinetics of such processes are not favorable. For example, while endergonic photoionization can take place inefficiently from S_1 which has a lifetime of 6 ns, it does not take place from T_2 even though S_1 and T_2 are nearly of the same energy since the shorter T_2 lifetime does not allow photoionization to compete. Therefore, the T_2 state relaxes back to T_1 before any competing process can take place. Since the nanosecond response time of our detection system does not allow observation of this T_1 depletion and recovery cycle, no change in the triplet decay kinetics or transient absorption spectrum would be expected.

Two-Laser Photochemistry of Anthracene with Electron Acceptors:

a) Ethyl bromoacetate. In order to confirm that electron transfer takes place from anthracene T_2 by observation of the radical cation spectrum, ethyl bromoacetate (EBA) was chosen as an electron acceptor. EBA is known to undergo rapid dissociation following electron capture to give bromide ion and ethoxycarbonylmethyl radical. Furthermore, substitution of the literature values for the oxidation and reduction potentials of anthracene and EBA into the Rehm-Weller equation indicates that electron transfer from either the S_1 or T_2 states of anthracene is exergonic. Figure 1 (square symbols) shows the transient absorption spectrum obtained following one-laser (UV) photolysis of a solution of anthracene in MeCN with added 1M EBA (spectrum was obtained 1.5 μs after the excimer laser pulse). In addition to the T-T absorption band (λ_{max} 425 nm) the anthracene radical cation absorption is also observed at λ 720nm. The absorption due to the radical cation is significantly enhanced when compared to the absorption in the absence of EBA thus confirming the participation of EBA in the oxidation of anthracene. Fluorescence quenching with EBA ($k_q = 5.0 \times 10^7$ $M^{-1} s^{-1}$) and the lack of triplet T_1 quenching indicate that one-photon cation radical production takes place at least partially through the singlet manifold.

The role of T_2 in the oxidation of anthracene was investigated by performing a two-laser experiment on a solution of anthracene in MeCN with added 1M EBA. Figure 1 (round symbols) also shows the transient absorption spectrum obtained 1.5 μs after the excimer laser pulse, and 500 ns after the dye laser pulse, i.e. at the same time as in the one-laser spectrum. No new absorption bands are produced by the dye laser. However, the absorbance at 720 nm due to the anthracene radical cation is approximately twice the value obtained in the one-laser experiment.

Figure 2 gives the kinetic behavior of this system under two-laser photolysis. Figure 2a shows the dye laser-induced bleaching of the T-T absorption at 430 nm. This bleaching indicates that the upper triplet state produced by absorption of the dye laser pulse decays by a process or processes that do not regenerate the T_1 state. Figure 2b shows the concomitant jump in the radical cation absorption. Thus, it appears that triplet T_2 decay leads to radical cation production. Since the yield of back intersystem crossing ($T_2 \rightarrow S_1$) in unsubstituted anthracene is very small,[25-28] dye laser enhanced production of radical cation must take place via interaction of EBA with T_2. This observation also indicates that at least a minor amount of the radical cation produced in the UV (one) laser experiment is via quenching of T_2.

b) Benzonitrile. In order to investigate anthracene upper triplet state processes with a non-dissociative electron acceptor, benzonitrile (BN) was used as a quencher in place of EBA. While the reduction potential of BN is more negative than that of EBA, electron transfer from anthracene T_2 is still approximately thermoneutral. When a solution of anthracene in MeCN with added 1M BN was irradiated with a UV laser, a transient absorption spectrum showed the formation of the anthracene triplet state. However, unlike the EBA experiment, no anthracene radical cation absorption was detected. Similarly, when a two-laser experiment was performed, extensive bleaching of the triplet-triplet absorption band was observed, but no radical cation absorption was detected. In order for electron transfer to take place without the detection of radical cation, in-cage back electron transfer (BET) must be fast. In addition, if triplet bleaching is due to electron transfer, T -> S intersystem crossing in the triplet geminate radical ion pair (RIP) must precede BET, otherwise the T_1 state would be regenerated and no bleaching would be detected. (It should be noted, however, that our observations do not rule out BET from the triplet RIP; it is

just that this process would be invisible on the time scale of our experiment). Rate constants for cage escape have been measured in a variety of radical ion pairs and found to be in the range of $10^8 \, M^{-1} s^{-1}$. If cage escape is of a similar rate in our system, the rate constant for ISC must be ca. 10^9 since the lack of observed radical cation indicates that cage escape is not a competitive process.

In order to test this hypothesis, we have carried out a two-laser experiment in which the sample was placed in a magnetic field ($H = 300$ G). Under these conditions ISC should be less efficient, possibly leading to enhanced cage escape and observation of radical cation. Unfortunately, no radical cation absorption was observed. It is possible that a larger magnetic field is required in order to slow the ISC rate sufficiently to allow cage escape to compete. Furthur experiments are planned with a larger magnet.

Triplet-triplet energy transfer is also a possible T_2 deactivation process since E_{T1} for BN is 77 kcal/mol. Although energy transfer from anthracene T_2 would be slightly endergonic under these conditions, the high concentration of BN could still lead to a large rate. In order to test for the possibility of energy transfer, a two-laser experiment was carried out using 1M 1,2-dimethoxybenzene (DMB) in place of BN. DMB is a much poorer electron acceptor than BN while its T_1 energy is 70 kcal/mol, making energy transfer from anthracene T_2 to DMB exergonic by 5 kcal/mol. Thus, triplet bleaching should be primarily due to energy transfer. Indeed, the magnitude of bleaching in DMB could be regarded as an upper limit for BN if *only* energy transfer occurs. In fact, we found the magnitude of bleaching with DMB much smaller than with BN. When this transient evidence is considered along with the fact that no stable photoproducts were detected by GC-MS, it is probable that the major process responsible for triplet bleaching in the presence of BN is electron transfer and

furthermore that the lack of new transient or stable products is due to rapid in-cage BET.

c) *Acrylonitrile and Fumaronitrile.* One- and two-laser studies, similar to those using BN, were performed with 1M acrylonitrile (AN) as quencher in MeCN. In both the one-laser (UV) and two-laser experiments T-T absorption was observed but there was no evidence for the production of radical cation, even in the presence of the 300 G magnetic field. Under two-laser irradiation, dye laser induced bleaching was detected. Product studies indicated that in both the one- and two-laser experiments a stable photoproduct, dibenzobicyclo[2.2.2]octa-5,7-diene-2-carbonitrile, was formed. However, ca. four times as much product was detected in the two-laser experiment as in the one-laser experiment. Substitution of an equimolar quantity of fumaronitrile for AN led to qualitatively the same results. Acrylonitrile has been reported to quench the S_1 state of naphthalene and anthracene by cycloaddition reactions. While the authors identified the product of naphthalene quenching to be the 2 + 2 cycloadduct, they did not identify the product of anthracene quenching.

Since BN and AN have similar reduction potentials, we assume that electron transfer from T_2 is a major decay pathway. The triplet RIP formed by electron transfer could then collapse to the 4 + 2 cycloadduct. A concerted cycloaddition, the usual pathway for thermal Diels-Alder reactions, would not be possible for the triplet RIP. However, if rapid ISC takes place as we have suggested for the anthracene/BN system, there would presumably be no restriction on concerted cycloaddition from the singlet RIP; reaction of diene radical cations with neutral dienophiles appears to follow such a path.

Alternatively, the triplet RIP could undergo sequential bond formation via the triplet 1,6-biradical **II** which could subsequently ring close after ISC.

CN

H

II
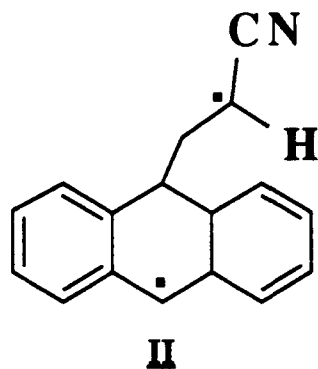
Given that the anthracene S_1 and T_2 states are nearly isoenergetic and that the lifetimes are 6 ns and ~200 ps, respectively, it may appear unusual that the bimolecular interaction of AN with the two-photon transient, anthracene T_2, leads to a greater amount of cycloaddition product than its interaction with S_1. However, if one considers that the dye laser has a much longer pulse duration and considerably larger pulse energy than either of the UV sources used, it is not surprising that more cycloaddition product is observed under two-laser irradiation.

Triplet-triplet energy transfer (T_2 (anthracene) ->AN) is also a feasible T_2 deactivation pathway This process is exothermic by ca. 18 kcal/mol (E_{T_1}(AN) = 58 kcal/mol). Similar energy transfer processes have been reported for a variety of systems including 9,10-dibromoanthracene (E_{T_2} = 74.6 kcal/mol) in the presence of 1,3-octadiene (E_{T_1} ~ 58 kcal/mol). Since T-T absorption for ^{3}AN* is not observable under our experimental conditions we would not expect dye laser excitation of the anthracene triplet followed by energy transfer to provide new transient species. We have also carried out two-laser experiments with anthracene in MeCN in the presence of 1,3-cyclohexadiene (E_{T_1} ~ 53 kcal/mol) and observed bleaching similar to that observed for AN. Thus, energy transfer could be competitive with electron transfer.

Conclusions

When EBA was used as a T_2 quencher, UV laser irradiation alone resulted in the production of anthracene radical cation, presumably as a result of both S_1 quenching and T_2 quenching following $S_1 \rightarrow T_2$ ISC. The radical cation was identified based on literature values, on its greater stability in polar vs nonpolar solvents, and on its reactivity with Br^-, a known cation scavenger. Dye laser-induced bleaching of the T-T absorption was accompanied by enhanced production of the radical cation via reaction of T_2.

The anthracene T-T absorption is also bleached in two-laser experiments with both BN and DMB in MeCN. These results indicate that both energy transfer and electron transfer are responsible for T_2 deactivation. The failure to detect anthracene radical cation even in the presence of an external magnetic field is likely due to a large triplet-singlet ISC rate in the geminate RIP which results in a large rate for BET.

In the presence of acrylonitrile and fumaronitrile, T_2 decays by a 4+2 cycloaddition reaction as is evidenced by the dye laser-induced bleaching of the T-T absorption, and the observation by GC-MS of the cycloaddition products. Two-laser experiments with 1,3-cyclohexadiene and 1,3-cyclooctadiene which have T_1 energies similar to acrylonitrile and fumaronitrile indicate that tripet-triplet energy transfer is also a possible T_2 decay pathway. While electron transfer is also thermodynamically feasible based on the known redox data for anthracene, acrylonitrile and fumaronitrile, transient evidence for the production of radical ions was not obtained. Again, a large rate for BET is likely responsible for this absence. It thus appears that when electron transfer does take place efficient in-cage ISC and BET prevent the production of free radical ions. Quantum yield experiments are currently being carried out in order to quantify these T_2 decay pathways.

II. Intramolecular Photoelectron Transfer in Molecules With Saturated and Unsaturated Acceptor Donor Bridges

The second section describes the synthesis and photophysical behavior of compounds in which the electron donor and acceptor are linked by one- and two-carbon bridges. The two-carbon bridges were both saturated and unsaturated. Although the unsaturated compounds were originally made only as synthetic intermediates they proved to have very interesting photophysical properties in their own right.

Part 1 describes the synthesis of the compounds, part 2 their photophysical behavior.

1. Synthesis of Bridged Donor/Acceptor Compounds

2-(3,4 -Dimethoxybenzoyl)fluorene [1] :

To a 100 ml flask was added 3,4-dimethoxybenzoic acid (7.28g, 0.04mol), DMF (2-3 drops) and thionyl chloride (28ml, 0.38mol). The solution was heated under gentle reflux for 40min, and the excess thionyl chloride removed under vacuum, leaving a solid (8.25g). The solid was dissolved in CS_2 (80ml), then fluorene (5.5g, 0.04mol) was added, followed by slow addition of aluminum chloride (5.3g, 0.04mol). The mixture was heated under reflux for 2 hr, then hydrolyzed with aqeuous HCl and the product extracted into chloroform. The solution was dried with $MgSO_4$, and the solvent evaporated. The crude solid was recrystallized from methanol/chloroform (10/1) to give 2-(3,4-dimethoxybenzoyl) fluorene (5.32g, 40%) , m.p. 151.0-153.5^{0}C; ν_{max} (KBr) 1645 (C=O) cm^{-1}; ^{1}H NMR (CDCl3) δ 3.96 (s, 2H, CH$_2$), 3.98 (s, 6H, CH$_3$), 6.90-6.94 (m, 3H, ArH), 7.4-8.0 (m, 7H, ArH).

2- (3,4-Dimethoxybenzyl)fluorene [2] :

To a 250ml flask was added 2-(3,4-dimethoxybenzoyl)fluorene (3.0g, 9mmol), sodium borohydride (3.0g), aluminum chloride (6.0g) and THF (150ml). The mixture was heated under reflux for 12 hr. After the solution had cooled, 400 ml of water was added. The product was extracted with benzene. The benzene was dried and the solvent evaporated; the product was recrystallized from methanol to give 2-(3,4-dimethoxybenzyl)fluorene (1.2g, 41%), m.p. 90.0-91.0^{0}C; ^{1}H NMR (CDCl3) δ 3.83 (s, 2H, CH$_2$), 3.86 (s, 2H, CH$_2$), 4.0 (s, 6H, OCH$_3$), 6.7-6.8 (m, 3H, ArH), 7.2-7.7 (m, 7H, ArH).

2-(3,4-Dimethoxybenzyl)-9-fluorenone [3] :

To a flask was added 2-(3,4-dimethoxybenzyl)fluorene (1g, 3mmol), pyridine (30ml), and Triton B solution (10ml). The mixture was stirred for 45 min at room

temperature, then acetic acid was added until the color changed to golden yellow. The solution was poured into large amount of water, giving a yellow precipitate which was isolated by filtration. The crude product was recrystallized from methanol to give 2-(3,4-dimethoxybenzyl)-9-fluorenone (0.42g, 42%), m.p. 106.0-107.0°C; ν_{max} (KBr) 1715 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.84 (d, 6H, OCH$_3$), 3.93 (s, 2H, CH$_2$), 6.7-6.8 (m, 3H, ArH), 7.2-7.6 (m, 7H, ArH).

2-Benzoylfluorene [4]:

To a 100 ml flask was added fluorene (1.66g, 10mmol), benzoyl chloride (1.16ml, 10mmol), and CS$_2$ (20ml), followed by aluminum chloride (1.33g, 10mmol) added slowly. The mixture was heated under reflux for 2 hr, cooled and chloroform added to dissolve the solid. Aqueous HCl was used to wash the organic layer, which was dried, the solvent evaporated and the product recrystallized from ethanol to give 2-benzoylfluorene (2.2g, 82%), m.p. 110.0-113.0°C; ν_{max} (KBr) 1640 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.92 (s, 2H, CH$_2$), 7.2-8.0 (m, 12H, ArH).

2-Benzylfluorene [5] :

The same procedure as for compound [2] was followed, yield 75%, m.p. 94.0-95.0°C; ^{1}H NMR (CDCl$_3$) δ 3.80 (s, 2H, CH$_2$), 4.02 (s, 2H, CH$_2$), 7.22-7.89 (m, 12H, ArH).

2-Benzyl-9-fluorenone [6] :

The same procedure as for compound [3] was followed, yield 50%, m.p. 70.0-72.0°C; ν_{max} (KBr) 1725 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) d 3.99 (s, 2H, CH$_2$), 7.18-7.84 (m, 12H, ArH).

9 - fluorenone - 2-carboxaldehyde [7] :

Fluorene-2-carboxaldehyde (5g, 26mmol) and 2,2-dimethylpropane-1,3-diol (2.8g, 27mmol) were heated under reflux in toluene (50 ml) in the presence of a small quantity of 4-toluenesulphonic acid. Water was removed by the Dean - Stark method and after work up, the residue was recrystallized from methanol to give 2-(5,5-dimethyl-1,3-dioxan-2-yl)fluorene (6.0g, 83%), m.p. 147.5-148.5^{0}C; ν_{max} (KBr) 1100 (C-O-C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.82 (s, 3H, CH$_3$), 1.34 (s, 3H, CH$_3$), 3.7-3.9 (m, 6H, CH$_2$), 5.47 (s, 1H, CH), 7.29-7.79 (m, 7H, ArH).

Pyridine (54ml) was added to commercial 40% Triton B in methanol (54ml) and the solution concentrated to 50ml. The 2-(5,5-dimethyl-1,3-dioxan-2-yl)fluorene (6.0g,0.02mol) in pyridine (43 ml) was added dropwise to the Triton B solution over a period of 15 min. Oxygen was bubbled through the stirred mixture during the addition and for the subsequent 30 min. When the color of the mixture changed to dark green, glacial acetic acid was added until the color of the mixture changed to golden brown. Then the solution was poured into water and the mixture filtered to give 2-(5,5-dimethyl-1,3-dioxan-2-yl)fluorenone (5.1g, 81%), m.p. 117.0-118.0^{0}C; ν_{max} (KBr) 1720 (C=O) , 1150 (C-O-C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.81 (s, 3H, CH$_3$), 1.30 (s, 3H, CH$_3$), 3.63-3.81 (m, 4H, CH$_2$), 5.39 (s, 1H, CH), 7.29-7.83 (m, 7H, ArH).

The 2-(5,5-dimethyl-1,3-dioxan-2-yl)fluorenone (5.1g, 17mmol) was hydrolysed by being heated under reflux with conc. HCl (3.5ml) in 75% aqueous dioxane (47 ml) for 3.5 hr. On cooling, the solution yielded a solid which was filtered and recrystallized from glacial acetic acid to give 9-fluorenone-2-carboxaldehyde (3.1g, 86%), m.p. 205.5-206.0^{0}C; ν_{max} (KBr) 1720(C=O) and 1680(CH=O) cm^{-1}; ^{1}H NMR(CDCl$_3$) δ 7.27-8.16(m, 7H, ArH), 10.03(s, 1H, CHO).

3,4-Dimethoxybenzyl chloride [8] :

To a 100 ml flask was added 3,4-dimethoxybenzyl alcohol (10 ml, 68 mmol), and dry ether (20 ml), and HCl gas was bubbled into the stirred solution. After 4 hr, the

solvent was evaporated and CHCl₃ used to extract the product. The extract was washed with water and NaHCO₃, dried and the solvent evaporated. The residure was chromatographed on silica using hexane/ethyl acetate (10/1). The first fraction (1000 ml) gave 3,4-dimethoxybenzyl chloride(2.2g, 17%), m.p. 46.0-47.0^{0}C; ^{1}H NMR(CDCl₃) δ 3.85 (d, 6H, OCH₃), 4.54(s, 2H, CH₂), 6.77-6.88(m, 3H, ArH).

3,4 - Dimethoxybenzyltriphenylphosphonium chloride [9] :

To a 100ml flask was added dry toluene (30ml), triphenylphosphine (3.8g, 0.014mol), and 3,4-dimethoxybenzyl chloride (2.2 g, 0.014 mol). The solution was heated under reflux for 6 hr and cooled. The solid was isolated by filtration , washed with ether and dried in vacuo to yield 3,4-dimethoxybenzyltriphenylphosphonium chloride (2.28g, 43%), m.p. 212.0 - 213.5 ^{0}C; ^{1}H NMR (CDCl₃) δ 3.52 (s, 3H, OCH₃), 5.40 (d, 2H, CH₂), 6.62 - 6.80 (m, 3H, ArH), 7.62 - 7.81 (m, 15H, ArH).

2-(2-(3,4-Dimethoxyphenyl)ethenyl)-9-fluorenone [10] :

To a 250 ml three-necked flask under N₂ was added 9-fluorenone-2-carboxaldehyde (1.27 g 6.1 mmol) in 25ml pyridine. Then 3,4-dimethoxybenzyltriphenylphosphonium chloride (2.74 g, 6.1 mmol) dissolved in 70ml EtOH, was added dropwise to the flask with stirring. Sodium (0.16g) in 41 ml EtOH was added dropwise to the flask. The mixture was stirred overnight at 60^{0}C, then cooled and the solid isolated by filtration, and acetone extraction. The solvent evaporated and the product recrystallized from acetone to give 2-(2-(3,4-dimethoxyphenyl)ethenyl)-9-fluorenone (0.61g, 30%), m.p. 171.0 - 172.0^{0}C; ν$_{max}$ (KBr) 3050, 1715 (C=O), 1600 cm^{-1}; ^{1}H NMR (CDCl₃) δ 3.80 (d, 6H, OCH₃), 6.98 (d, 2H, olefinic H), 7.17 - 7.85 (m, 10H, ArH).

2-(2-(3,4-Dimethoxyphenyl)ethyl)-9-fluorenone [11] :

2-(2-(3,4-Dimethoxyphenyl)ethenyl)-9-fluorenone (100mg, 0.3mmol), 10% palladium on activated carbon (4mg) and THF (10ml) were stirred for 4 h under H_2 at ambient temperature. The solution was isolated by filtration. The solvent was evaporated and the product recrystallized from hexane/chloroform (10/1) to give 2-(2-(3,4-dimethoxyphenyl)ethyl)-9-fluorenone (43mg, 43%), m.p. 100.0 - 100.5^{0}C; υ_{max} (KBr) 1715 (C=O) cm^{-1}; ^{1}H NMR (CDCl3) δ 2.62 (s, 4H, CH2), 3.41 (d, 6H, OCH3), 6.65 - 6.85 (m, 3H, ArH), 7.25 - 7.75 (m, 7H, ArH).

Benzyltriphenylphosphonium chloride [12] :

To a flask was added benzyl chloride (3.6ml, 0.03mol), triphenylphosphine (7.7g, 0.03mol) and CHCl3 (35ml). This solution was heated under reflux for 4 hr and cooled to room temperature. About 120ml ether was added after which a white precipitate formed immediatedly, which was filtered and dried in vacuo; benzyltriphenylphosphonium chloride (9.5 g, 81%), m.p. 315.0 - 319.0^{0}C; ^{1}H NMR (CDCl3) δ 5.3 (d, 2H, CH2), 6.7 - 7.7 (m, 20H, ArH).

2-(2-Phenylethenyl)-9-fluorenone [13] :

The same procedure as for compound [10] was followed. Yield 27%, m.p. 178.0 - 179.0^{0}C; ν_{max} (KBr) 1715 (C=O) cm^{-1}; ^{1}H NMR (CDCl3) δ 7.3 -7.9 (m, olefinic H and ArH).

2-(2-Phenylethyl)-9-fluorenone [14] :

The same procedure as for compound [11] was followed. Yield 80%, m.p. 79.5 - 80.0^{0}C; ν_{max} (KBr) 1710 (C=O) cm^{-1}; ^{1}H NMR (CDCl3) δ 2.95 (s, 4H, CH2), 7.15 - 7.72 (m, 12H, ArH).

9-Fluorenone-4-carboxaldehyde [15] :

To a three-necked flask under N_2 was added 9-fluorenone-4-carbonyl chloride (0.5g, 0.5mmol) and 20 ml of dry diglyme. The solution was stirred and the flask was cooled to -78^{0}C. Lithium tri-tert-butoxyaluminohydride (4ml, 0.5 M solution in diglyme) was added at such a rate as to maintain the internal temperature below -68^{0}C when the bath temperature reached -72^{0}C. After addition was completed, the mixture was stirred at -78^{0}C for 1 hr.

The cold reaction mixture was poured slowly with stirring into beaker which contained 10 ml conc. HCl, 20 ml of sat NaCl and 10 g of ice. A yellow precipitate formed, which was isolated by filtration. The product was recrystallized from 95% ethanol to give

9-fluorenone-4-carboxaldehyde (0.18g, 42%), m.p. 165.0 - 168.0^{0}C; v_{max} (KBr) 1720 (C=O), 1705 (CH=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.5 - 8.5 (m, 7H, ArH), 10.5 (s, 1H, CHO).

4-(2-(3,4-Dimethoxyphenyl)ethenyl)-9-fluorenone [16] :

The same procedure as for compound [10] was followed.Yield 30%, m.p. 125.0 - 126.0^{0}C; v_{max} (KBr) 1715 (C=O), 1150 (C - O - C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.90 (d, 6H, OCH$_3$), 6.72(m, 2H, olefinic H), 7.08 - 7.70 (m, 10H, ArH).

4-(2-(3,4-Dimethoxyphenyl)ethyl)-9-florenone [17] :

The same procedure as for compound [11] was followed. Yield 64%, m.p. 124.0 - 125.0^{0}C; v_{max} (KBr) 1710 (C=O), 1150 (C - O - C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.9 - 3.3 (m, 4H, CH$_2$), 3.85 (d, 6H, OCH$_3$), 6.7 - 6.9 (m, 3H, ArH), 7.2 - 7.8 (m, 7H, ArH).

4-(2-Phenylethenyl)-9-fluorenone [18] :

The same procedure as for compound [10] was followed. Yield 40%, v_{max} (KBr) 1710 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.9 - 7.9 (m, 14H, olefinic and ArH).

4-(2-Phenylethyl)-9-fluorenone [19] :

The same procedure as for compound [11] was followed. Yield 70%, m.p. 72.0 - 73.0^{0}C; ν_{max} (KBr) 1710 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.0 - 3.2 (m, 4H, CH$_2$), 7.1 - 7.7 (m, 12H, ArH).

2. Photophysical Behavior of Bridged Donor/Acceptor Compound: Intramolecular Electron Transfer.

Intramolecular electron transfer is expected to be more efficient than intermolecular electron transfer due to the effectively higher local concentration of the acceptor moiety. Also, electron transfer rates can be further accelerated if the donor and acceptor groups are spaced rigidly by a hydrocarbon framework.

Thus, we have synthesized 2-(2-(3,4-dimethoxy-phenyl)ethyl)-fluoren-9-one, (11) and 2-(2-phenylethyl)-fluoren-9-one, (14). Both (11) and (14) contain electron donor and acceptor groups separated by a saturated 2-carbon bridge.

Laser flash photolysis experiments performed on (11) yielded a T-T absorption spectrum and triplet lifetime very similar to that of fluorenone itself under similar conditions although the absorption was red-shifted slightly.

When two-laser experiments were carried out on (11) in order to test for electron transfer, the decay traces obtained were qualitatively the same as the one-laser decays; i.e., there was no triplet bleaching observed nor was there evidence for any new transients formed. This indicates that two photon-induced electron transfer in (11) is not an efficient process compared to alternative deactivation pathways. Inefficient electron transfer may be due to either weak T-T absorption or unusually fast $T_n \rightarrow T_1$ internal conversion.

More interesting results were obtained with *cis*-2-(2-phenyl-ethenyl)-fluorenone (*cis* -13), *trans*-2-(2-phenyl-ethenyl)fluorenone (*trans*-13), and 2-phenylethenyl-fluorenone (*yne*-13). The absorption spectra of all three compounds resembled that of fluorenone and showed little solvent sensitivity. Their fluorescence spectra displayed substantial Stokes shifts (ranging from 3800 to 5500 cm^{-1}), and moderate solvatochromic shifts between cyclohexane (CH) and acetonitrile (MeCN): *cis*-13, 1436 cm^{-1}; *trans*-13, 1470 cm^{-1}; *yne*-13, 1187 cm^{-1}.

These data suggest that the excited states are substantially more polar than the ground states and that solvent relaxation is a major contributor to the Stokes shifts.

The alkene stereoisomers undergo facile photoisomerizaion in CH, benzene (PhH), CHCl$_3$ and MeCN when photolyzed in a Rayonet reactor with 300 or 350 nm lamps, or with a Hanovia lamp equipped with a filter solution to cut off light with λ < 400 nm. The photostationary *trans/cis* ratio shows a very marked dependence on concentration. At 4 x 10^{-2} M the only product is the trans-isomer regardless of starting isomer, solvent, wavelength or atmosphere (N$_2$ or air), within the limits of detection. (The relative concentrations were determined by NMR, with which 2% of the *cis*-isomer could be seen.) However, photolysis of trans-13 in CH at 300 nm under N$_2$ at a concentration of 2 x 10-4 M leads to a 65:35 *trans/cis* mixture. In MeCN the ratios are 65:35 (*trans*) and 63:37 (*cis*) under N$_2$, and 72:28 in air.

The evidence points to a predominantly triplet isomerization mechanism, despite the polarity of the initially-formed excited states. Increasing proportions of *trans*- isomer with increasing concentration of starting alkene is characteristic of quantum chain processes proceeding on the triplet surface. The higher quantities of *trans*- isomer and slower rates of photo-equilibration under air also accord with a triplet process. We found ϕ_F for either *cis*- or *trans* -13 to be 0.07-0.08 in CH. ϕ_{ISC} for fluorenone is 0.93, and if we assume a similar value for 13 then virtually all excited states that do not fluoresce should cross over into the triplet manifold in nonpolar solvents.

Laser flash photolysis (LFP) provided further support for the triplet hypothesis. LFP of *trans* -13 in CH at 3 x 10^{-5} M under N$_2$ (308 nm, 8 ns pulse, 40 mj) produces a transient with λ_{max} at 470 nm ($\tau \sim$ 4 μs) which is strongly quenched by O$_2$. We assume this to be the spectrum of the planar *trans* triplet.

This spectrum also displays a shoulder at 440 nm. When *cis*-13 is photolyzed under the same conditions the 440 nm absorption is much enhanced relative to the 470 nm peak, by comparison with the *trans*-13 spectrum. It has previously been found that arylethylene *cis*-triplets always decay to the *trans*-triplets within the lifetime of the exciting pulse. We therefore believe that our 440 nm peak arises from a separate intermediate (*vide infra*).

In nonpolar solvents styrylfluorenones seemed to behave like simple arylethylenes despite the presence of the strongly electron-withdrawing fluorenonyl carbonyl group. Isomerization appeared to take place mainly via triplet intermediates although the data do not rule out a complimentary singlet pathway.

However, LFP in MeCN revealed an entirely different process under high energy conditions. Irradiation into the $S_1 \leftarrow S_0$ band of *trans*-13 with a dye laser tuned to 445 nm (300 ns, 52 mj; OD_{445} 0.5) gave no visible transient 1 µs after excitation. However, photolyses of samples with the same OD at the exciting wavelength using either a Nd/YAG laser (355 nm, 40 mj; $S_1 \leftarrow S_0$) or an excimer laser (308 nm, 40 mj; $S_n \leftarrow S_0$) produced a new transient with λ_{max} 440 and 580 nm, $\tau \sim 4$ µs.

Photolysis of the *cis*-isomer was equally instructive. Photolysis in dry MeCN under air at 308 nm gave evidence of both transients: the triplet at 470 nm and the new transient absorbing at 450 and 580 nm. As expected, the 470 nm signal decayed very rapidly; after 4 µs it was completely gone and the main absorption was at 580 nm. Photolysis in MeCN N_2 gave a broad absorption centered between 450 and 470 nm and little at 580 nm.

This new transient was not quenched by air but was sensitive to solvent additives. In "wet" MeCN (containing adventitious water) the 580 nm peak was decidedly more intense than the 440 one, whereas in "dry" MeCN they were more

nearly equal. Deliberate addition of water to the solvent (9:1 MeCN/H$_2$O) shortened the lifetime of the transient. Water was undoubtedly reacting nucleophilically, since Bu$_4$N$^+$ Br$^-$ quenched the transient at nearly the diffusion controlled rate. On the other hand, addition of a small quantity of CF$_3$COOH to the solvent (~ 0.5 M) extended the lifetime of the transient and caused a small blue shift of its long wavelength absorption. These experiments established the cationic character of the transient.

There was also strong evidence that the transient might be anionic as well. The peaks at 580 and 440 nm correspond closely with those reported for free fluorenone radical anion and its paramagnetic dimer, respectively. The growth of the 440 peak at the expense of the 580 peak as the solvent became less aqueous, as well as a blue shift of the 580 peak observed upon CF$_3$COOH addition, are in accord with this assignment.

We undertook to further support it by chemically quenching the postulated fluorenone radical anion fragment. Savéant has reported the biomolecular rate constant for electron transfer from the radical anion to CF$_3$I in DMF: k = 2.3 x 10^6 M^{-1} s^{-1}. Accordingly, we photolyzed a solution of trans-13 (3 x 10^{-4} M) in MeCN containing CF$_3$I (1.5 M) at 355 nm. Since CF$_3$I could quench the transient by promoting intersystem crossing as well as by reaction chemically, we carried out a completely parallel experiment in which CH$_3$I was substituted for CF$_3$I. As expected, both iodides shortened the transient lifetime. However, examination of the UV-vis spectra of the solutions before and after photolysis showed that only in the CF$_3$I solution had photolysis led to a chemical reaction.

If this transient does indeed have a fluorenone radical anion portion then the styrene unit must act as the electron donor, producing a styrene radical cation part. The energetics of formation of this radical zwitterion warrant comment. We can estimate its energy by using the E$_{1/2}$ values for styrene (+1.50 V) and

fluorenone (-1.245 V) measured in DMF vs SCE. Assuming that the zwitterion has a TICT structure requires that the energy of rotation around the styryl-fluorenonyl bond be added, which we assign a value of 5 kcal/mol. Thus, a minimum energy of 68 kcal/mol would be needed to reach this intermediate from the *trans*-13 ground state.

The S_1 energy of trans-13 is unknown but we can crudely estimate it by taking the difference between the absorption (434 nm) and emission (549 nm) maxima in MeCN. It equals 491 nm and amounts to 58 kcal/mol, 10 kcal shy of the minimum needed to reach the zwitterionic state. This would explain why the dye laser (445 nm) cannot produce this transient but the Nd/YAG (355 nm) and excimer (308) lasers can. It also means that the zwitterionic state is being populated from S_2 of *trans*-13. While singlet upper state reactivity that competes with internal conversion is relatively rare there is a precedent in TICT photochemistry. It appears that the TICT state of 9-morpholinoacridine can be directly populated from S_2 of the ground state.

The apparent longevity of our transient is plausible based on the data given so far. Its substantial energy above the ground state would slow down internal conversion, while the high chemical stability of the fluorenone radical anion would serve to enhance its lifetime. Mattay has been able to observe the radical anion using a 16 μs flash lamp. Finally, the role of the hypothesized dimer in stabilizing the transient should not be overlooked.

We assigned the 440 nm peak in the transient spectrum to a dimer, by analogy with the "paramagnetic dimer" which Mattay showed was the source of a 450 nm peak in the spectra of fluorenone radical anion in various organic solvents. Our dimer is precisely equivalent to the "bicimer" proposed to explain the TICT behavior of DCS.

If this assignment is accurate then our transient spectra indicate the formation of this dimer even in nonpolar solvents such as CH and PhCH3, in which no evidence for monomeric zwitterions is found (or would be expected). Furthermore, equilibrium formation of the dimer in polar solvents would serve as a means of stabilizing the monomer in them. Finally, the photolyses of *cis*-13 in MeCN yielded a transient very similar to, but distinct from, the transient produced from the *trans*-isomer. Since rotation about the double bond of styrene radical cations is relatively slow it is to be expected that the zwitterions produced form the stereoisomeric starting materials would have stereoisomeric structures.

Experiments are now in progress to further characterize the transients described here and to elucidate their role, if any, in the photoisomerization of *cis*- and *trans*-13. We are also attempting to detect the fluorescence to be expected from such long-lived species. If our energetic analysis is correct then the 540-550 nm fluorescence from the alkene isomers cannot arise from the zwitterion. We have shown that Bu4N$^+$ Br$^-$, which quenches the transient strongly, has only a weak effect on the static fluorescence of these compounds.

Since rapid rotation about the around vinyl-aryl bond is crucial to the competition between internal conversion and zwitterion formation, we are studying the photochemistry of *yne*-13. With its very low intrinsic rotational barrier, it should be a good precursor for zwitterionic transients.